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Magnetodynamic Effects on Outer-Sphere Electron-Transfer Reactions: A Paramagnetic Transition State

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The effect of the magnetic field on the rate of outer-sphere electron-transfer reactions has been investigated as a function of the field intensity, between 0 and 9 T, and at a given temperature. In complexes of d^6 metal ions, i.e., Ru(II) and Co(III), the rate constant exhibits a complex dependence on the field: a complexity associated with field-induced changes of the electronic matrix element and the activation energy. Changes in the activation energy have been investigated as a function of the temperature at a given field intensity. These measurements have shown that the magnetic susceptibility of activation has the large positive values that are expected for a strongly paramagnetic transition state. The magnetic field effects are discussed in terms of symmetry-determined selection rules for the coupling of the initial and final electronic states of the reactions.

Introduction

The magnetic-field-induced accelerations and decelerations of the rate of ground- and excited-state reactions involving inorganic and organic reactants have been the subject of a number of studies.[1-9] Recent work has shown that there are significant differences between those mechanisms by which the magnetic field perturbs the rate of reactions involving coordination complexes and those mechanisms applying to reactions between radicals or excited states of organic molecules.[1,2] For example, under intense magnetic fields, $0 < H < 6$ T the rate constant for the radiationless relaxation of (^{3}CT)-Ru(bpy)$_3^{2+}$ exhibits a linear dependence on the magnetic field instead of the quadratic dependence (eq 1) that

$$k(H) = (1/\hbar)|\langle\Psi_i|\hat{\mathcal{H}}_{v,so} + \hat{\mu}\vec{H}|\Psi_f\rangle|^2 \simeq k(0) + \mu^2H^2 \quad (1)$$

$$\hat{\mathcal{H}}_{v,so} = \text{vibronic, spin–orbit coupling operator}$$

$$\hat{\mu} = \text{magnetic dipole operator}$$

has been observed with excited states of organic molecules.[2,10-13] In this compound of a second-row transition-metal ion, the departure from the expected functional dependence has been attributed to a mechanism involving the electronic Zeeman-induced mixing of the ^{3}CT with other states of similar energies.[2]

A large body of work has also been done on the effect of the magnetic field over the rates of reactions involving the coalescence of two species in multiplet states, e.g., radical–radical and triplet–triplet annihilation reactions.[14-16] The mechanisms for such reactions assign the field's effect to the induced modification of electronic levels and transition probabilities. Magnetic interactions that determine the evolution from one spin state to another, e.g., from a triplet radical pair to a singlet radical pair, have been identified as the electronic Zeeman and the hyperfine coupling.[17-26] These mechanisms have proved to be very successful in accounting for all the experimental observations in thermal and photochemical reactions involving species where spin–orbit coupling and the orbital contribution to the electronic angular momentum are of insignificant consequence. Bimolecular reactions between coordination complexes, i.e., outer-sphere electron transfers, are not expected to fall within the previous class of reactions because of intrinsically strong spin–orbit couplings and large orbital contributions to the electronic angular momentum.[27-29] In addition, the CIDNP- and CIDEP-based mechanisms consider reactions proceeding under an almost diffusion-controlled rate while a large number of the outer-sphere electron transfers have activation energy limited rates.[21-26] In such cases, one expects that the effect of the magnetic field on the rate constant reflects the combined interactions of the field with the reactants (initial state), products (final state), and a given transition state (activation complex). This point can be expressed in a more quantitative manner with eq 2,[30] derived from the absolute rate theory. The subscript H

$$k_H = \kappa_H K^\ddagger{}_H \quad (2)$$

in eq 2 denotes that the activated complex pseudoequilibrium constant, $K^\ddagger{}_H$, and the transmission coefficient, κ_H, are both field-dependent parameters that contribute to the overall dependence of the specific rate constant, k_H, on the magnetic field. Insofar as the transmission coefficient must be calculated over the entire space of the reaction coordinate and in terms of the eigenfunctions for a given potential field, which includes the magnetic interactions, the dependence of this parameter in the magnetic field can be easily recognized.[30] The dependence of $K^\ddagger{}_H$ on the magnetic field can be associated with the field-induced change in the position of the reactants-activated complex pseudoequilibrium (eq 3),[30] where A, B, and AC‡ represent the

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AC}^\ddagger \qquad K^\ddagger{}_H = \exp(-\Delta G^\ddagger{}_H/RT) \quad (3)$$

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Table I. Polynomial Expansion Coefficients for the Fitting of $k(H)/k(0)$[a]

reactants[b]	a_1, T^{-1}	a_2, T^{-2}	a_3, T^{-3}	a_4, T^{-4}	$Q\Sigma_i\alpha_i e^{-E_i/RT}\Sigma_f\lvert V_{if}\rvert^2$, J	$\delta\chi^\ddagger$, J/T^2
$Co(NH_3)_6^{3+}$ + $Ru(NH_3)_6^{2+}$	-2.95×10^{-1}	1.57×10^{-1}	-2.81×10^{-2}	1.60×10^{-3}	1.3	2.4×10^2
$\{Co(NH_3)_6^{3+}, Cl^-\}$ + $Ru(NH_3)_6^{2+}$	-4.78×10^{-1}	3.45×10^{-1}	-7.69×10^{-2}	5.15×10^{-3}	1.8	3.9×10^2
$Co(NH_3)_6^{3+}$ + $Co(sep)^{2+}$	-8.04×10^{-1}	4.43×10^{-1}	-7.50×10^{-2}	3.91×10^{-3}		
$Co(en)_3^{3+}$ + $Co(sep)^{2+}$	-1.62×10^{-1}	4.19×10^{-2}	-1.48×10^{-2}	2.13×10^{-3}[c]		

[a] Coefficients defined in eq 12. [b] For experimental conditions see Figures 1 and 3. [c] Good fitting for $H < 6$ T.

reactants and activated complex, respectively, and $\Delta G^\ddagger_H$ is the activation energy in the presence of a magnetic field H. If one considers that the magnetic field changes the energy of a material in an amount that is proportional to the square of the magnetic field intensity, the activation energy $\Delta G^\ddagger_H$ is given in terms of the activation energy at zero field, $\Delta G^\ddagger_0$ (eq 4).[30-33] The proportionality constant, $\delta\chi^\ddagger$, is the (molar) activation magnetic susceptibility that is defined in eq 5 as a difference between the

$$\Delta G^\ddagger_H = \Delta G^\ddagger_0 - \delta\chi^\ddagger H^2/2 \qquad (4)$$

$$\delta\chi^\ddagger = \chi_{AC^\ddagger} - \chi_A - \chi_B \qquad (5)$$

magnetic susceptibilities of the activated complex and reactants respectively, i.e., in the same manner that is followed for the definition of other molar activation parameters.[30]

In this paper we report results on the effect of the magnetic field on the rate of outer-sphere electron transfers involving Co and Ru complexes. Such reaction rates have been investigated as a function of the field intensity at various temperatures in order to learn about the mechanism of the magnetic perturbation and the magnetic nature of the transition state.

Experimental Section

Reaction Rates Measurements. The rates of the reactions were measured for pseudo-first-order kinetics with one of the reactants 10-fold to 100-fold in excess with respect to the other reactant's concentration. In those reactions with such rates that optical density measurements could be carried out in a spectrophotometer, solutions were handled under anaerobic conditions by using the syringe procedure. Moreover, the accuracy of the measurements was optimized by adding a given volume of one reactant's solution to a weighted and deaerated sample of the other already placed in the reaction cell. The concentrations were calculated from the weight of the mixture, the known weight of one of the solutions, and the respective concentrations of the complexes in their stock solutions. A modified gastight spectrophotometer cell allowed us to place the reaction mixture inside the cavity of an American Magnetics superconducting magnet, which was able to generate magnetic fields between 0 and 9 T. Reaction mixtures in the cavity were kept at a constant temperature that experiences insignificant fluctuations, $\Delta T \leq 0.2$ °C, during the experiments. The reactions were followed at suitable wavelengths by reading the optical density with an error, $\delta OD = \pm 0.0002$. In individual determinations of the rate constants, the relative "most probable error" of the rate constants is 3%. The ratio, $k(H)/k(0)$, of the rate constants in a field H, $k(H)$, and in a zero field, $k(0)$, was calculated from an average of five to seven individual determinations with a standard deviation equal to or less than 3%.

Reactions whose rates were too fast for the procedure described above were investigated with a Dionex stopped-flow spectrophotometer modified for injection mixing inside the magnet's cavity. Magnetic-field-sensitive parts in the detection system, e.g., phototube and lamp monochromator, were removed an appropriate distance from the magnet and optically coupled to the reaction cell by means of fused silica fiber optics.

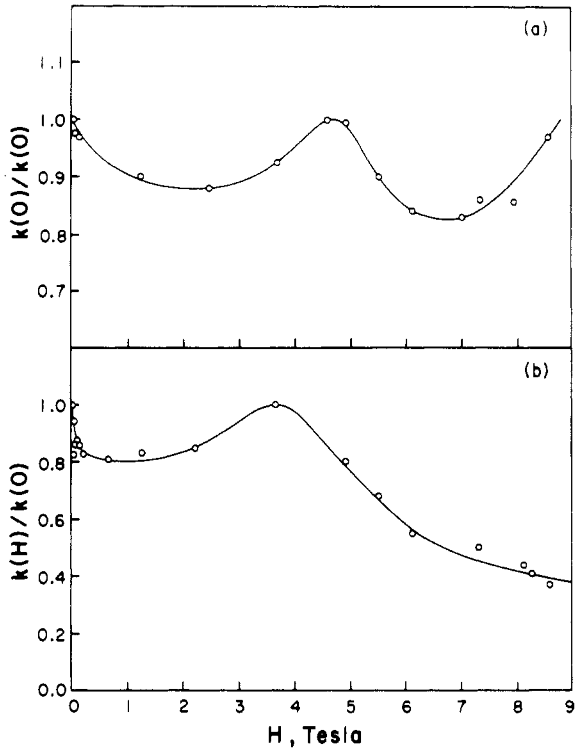


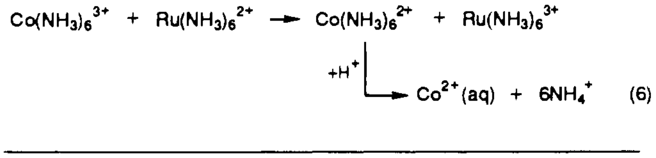
Figure 1. Dependence of the ratio $k(H)/k(0)$ of the rate constants $k(H)$ (under a given magnetic field) and $k(0)$ (under a zero field) on the magnetic field intensity. The $k(H)/k(0)$ values in (a) have been determined for the reduction of $Co(NH_3)_6^{3+}$ by $Ru(NH_3)_6^{3+}$ in acidic solutions, pH 3, with an ionic strength $I = 0.3$ M NaTFS and $T = 298.0$ K. The constants in (b) have been measured for the reduction of the ion pair $\{Co(NH_3)_6^{3+}, Cl^-\}$ with $Ru(NH_3)_6^{2+}$ in acidic solutions, pH 3, having an ionic strength $I = 0.3$ M NaCl and T = 290.0 K.

Materials. The compounds $[Ru(NH_3)_6](ClO_4)_3$, $[Co(NH_3)_6](ClO_4)_3$, and $[Co(NH_3)_5Cl](ClO_4)_2$ were available from previous work.[1,2] Alfa $[Ru(NH_3)_6](ClO_4)_2$ and $[Co(sep)](ClO_4)_3$ (sep = 1,3,6,8,10,12,16,19-octaazabicyclo[6,6,6]icosane] were purified according to literature procedures.[35,36] The purity of the compounds indicated above was established by means of their UV-Vis spectra.

Other materials were reagent grade and were used without further purification.

Results

Although the effect of the magnetic field on the rate of outer-sphere electron transfers was first investigated in the reaction between diamagnetic cobalt(III) and ruthenium(II) hexaammines (eq 6), such study was done under a narrow range of experimental conditions.[37]



$$Co(NH_3)_6^{3+} + Ru(NH_3)_6^{2+} \rightarrow Co(NH_3)_6^{2+} + Ru(NH_3)_6^{3+};\quad Co(NH_3)_6^{2+} \xrightarrow{+H^+} Co^{2+}(aq) + 6NH_4^+ \qquad (6)$$

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(31) Note that $\Delta G^\ddagger$ represents the difference between the respective standard free energies of the activated complex and the reactants.[30] Therefore, the effect of an electromagnetic field on such (dielectric and magnetically) polarizable material is to change its energy in

$$\omega = \int\int \vec{E}\, d\vec{D}\, dv + \int\int \vec{H}\, d\vec{B}\, dv$$

where the volume integrals are over all the space and the field integrals are from zero field to the final state. $\vec{E}$ and $\vec{H}$ are the electric and magnetic fields, respectively, while $\vec{D}$ and $\vec{B}$ are known respectively as electric displacement and magnetic induction vectors.

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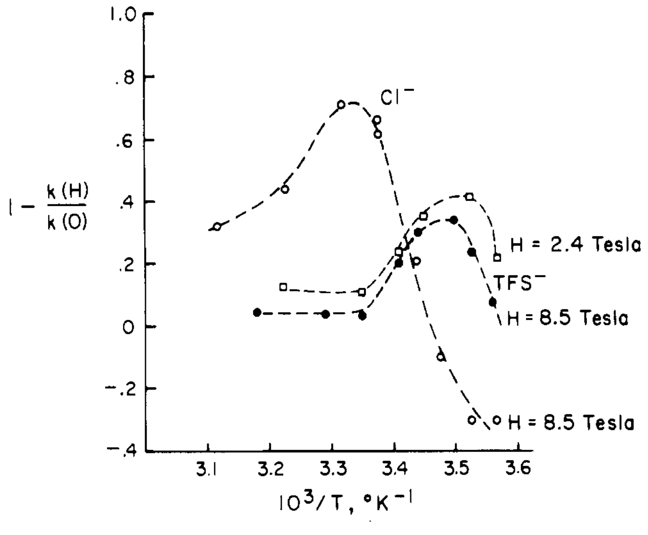


Figure 2. Temperature dependence of the ratio $k(H)/k(0)$ of the rate constant $k(H)$, determined at a field intensity H, to the rate constant $k(0)$, determined at a zero-field intensity. The counterions and respective field intensities used for the study of the reaction between $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ are indicated in the figure. For other conditions, see Figure 1.

In this work, the magnetic field effects were investigated at a constant temperature, $T = 298$ K, under medium conditions, pH 3 and $I = 0.3$ M in NaCl, where more than 99.0% of the Co(III) complex was ion paired with Cl^- (Figure 1).[38,39] The experimental results, expressed as a ratio $k(H)/k(0)$ of the rate constant, $k(H)$, measured under a field H to the rate constant, $k(0)$, in the absence of field, can be approximately fitted by a power series

$$k(H)/k(0) = 1 + \sum_{n=1}^{\infty} a_n H^n$$

truncated to a polynomial of a given degree on the magnetic field.[40] For example, a polynomial of the fourth degree on the magnetic field gives acceptable fittings of the experimental data (Figure 1 and Table I). Similar behavior has been observed under conditions, i.e., pH 3 and $I = 0.3$ M NaTFS, where the Co(III) complex must also be forming ion pairs with TFS^- (Figure 1 and Table I).[41-43] Despite the qualitative similarities between the dependences of $k(H)/k(0)$ on H shown in Figure 1 for the reactions of $Ru(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$, it must be noted that the polynomia fitting the data respectively collected with Cl^- and TFS^- counterions are significantly different and that the values of the coefficients dictate that such differences tend to be more pronounced with increasing fields, i.e., at fields $H > 5$ T.

Experiments carried out at a given field intensity (Figure 2) have shown that the effect of the magnetic field upon the reaction rate is temperature dependent. In solutions where $Co(NH_3)_6^{3+}$ is ion paired with TFS^- formation, the results collected over a temperature range, $289 < T < 323$ K, with the field intensities set at 3 and 8 T, respectively, are distributed according to curves that are dependent on the field intensity. The curve obtained in similar experiments with $\{Co(NH_3)_6^{3+},Cl^-\}$ ion pairs is largely displaced with respect to the curve determined for $Co(NH_3)_6^{3+}$ at the same field intensity.

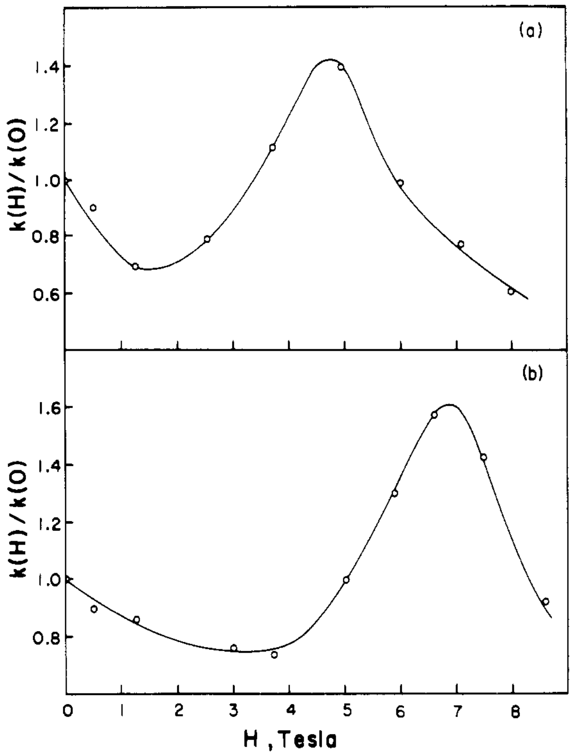
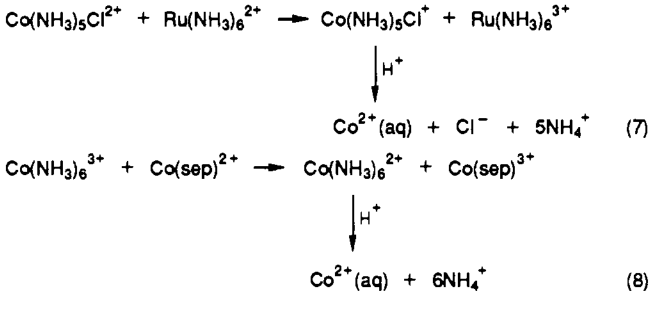


Figure 3. Dependence of the ratio $k(H)/k(0)$ on the magnetic field intensity. The $k(H)/k(0)$, values in the figure have been measured for the oxidation of $Co(sep)^{2+}$ with (a) $Co(NH_3)_6^{3+}$ and (b) $Co(en)_3^{3+}$. These reactions, eqs 8 and 9, were investigated in acidic solutions, pH 3, having an ionic strength $I = 0.3$ M NaTFS.

One of the questions risen by the experimental observations reported above is whether they have a general validity; i.e., will electron transfer reactions of related coordination compounds exhibit similar dependencies on the magnetic field? In this regard we have investigated several reactions of Co(III) complexes, eqs 7–9, and found that their rates experienced field-induced perturbations (Figure 3) that are similar to those observed in the reaction between cobalt(III) and ruthenium(II) hexaammines (eq 6). A difference between these reactions must be noted; while the reactants of eq 6 are diamagnetic, $Co(sep)^{2+}$ in eqs 8 and 9 has a multiplet (paramagnetic) ground state.[44,45]



$$Co(NH_3)_5Cl^{2+} + Ru(NH_3)_6^{2+} \rightarrow Co(NH_3)_5Cl^{+} + Ru(NH_3)_6^{3+}$$
$$\downarrow H^+$$
$$Co^{2+}(aq) + Cl^- + 5NH_4^+ \qquad (7)$$

$$Co(NH_3)_6^{3+} + Co(sep)^{2+} \rightarrow Co(NH_3)_6^{2+} + Co(sep)^{3+}$$
$$\downarrow H^+$$
$$Co^{2+}(aq) + 6NH_4^+ \qquad (8)$$

$$Co(en)_3^{3+} + Co(sep)^{2+} \rightarrow Co(en)_3^{2+} + Co(sep)^{3+} \qquad (9)$$

Discussion

The results reported above and in a previous work show that magnetodynamic effects on outer-sphere electron-transfer reactions

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(44) The results collected with reactions of $Co(sep)^{2+}$ are presented here for comparison with reactions between diamagnetic Co(III) and Ru(II) complexes. Insofar as the theoretical treatment of the reactions involving paramagnetic ions is more complex than the one applied in this work to reactions between diamagnetic species, the discussion of their properties will be deferred.[45]

(45) Ronco, S.; Ferraudi, G. Work in progress.

have complex dependences on the field intensity, dependences that have been empirically described by means of polynomia with higher orders on the magnetic field intensity. The polynomia for the dependence of $k(H)$ on H show in a quantitative manner that the magnetic-field perturbations are not only specific for a given reaction but also reflect subtle interactions with species in the second coordination sphere, i.e., species which may be forming ion pairs with a given reactant. Moreover, one feature that emerges from the field effects on the rates of the investigated reactions is that the reactants are not required to be in paramagnetic electronic states as a precondition for the observation of field-induced perturbations. These observations are rationalized in the following sections by using established theories for the rate of outer-sphere electron-transfer reactions.[46-54]

(a) General Considerations about Magnetic Field Effects. Although eq 2 has a general validity in reaction kinetics, it is more convenient to interpret the experimental results of this paper according to the theoretical models proposed for outer-sphere electron transfers in coordination complexes.[49-53] The quantum-mechanical theory provides a good starting point for the treatment of the magnetic field effects. Indeed, the rate constant of an electron-transfer reaction (eq 10) can be expressed in terms of

$$\left(k = A\frac{\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}|V_{\mathrm{if}}|^2}{\sum_{\mathrm{i}}\alpha_{\mathrm{i}}^0e^{-E_{\mathrm{i}}^0/RT}}\right)e^{-\Delta G^{\ddagger}/RT} \qquad (10)$$

a factor A, which is independent or nearly independent of the magnetic field, a Boltzmann-weighted electronic matrix element V_{if} and an exponential factor dependent on the Franck–Condon and solvent reorganization energies, $\Delta G^{\ddagger}$, where zero superscripts indicate zero-field values.

In the deduction of eq 10, we have assumed that the distinct reorganization energies $\Delta G_{\mathrm{if}}^{\ddagger}$, associated with transitions from an initial state i to a final state f, can be replaced by an average, and therefore factorizable, reorganization energy $\Delta G^{\ddagger}$. Also we have used the approximation[32,33]

$$Q(H) = 1/\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT} \simeq Q(0) = 1/\sum_{\mathrm{i}}\alpha_{\mathrm{i}}^0e^{-E_{\mathrm{i}}^0/RT} = Q$$

for the partition functions, $Q(H)^{-1}$, in presence of the magnetic field, and $Q(0)^{-1}$, in the absence of it.

Since $\hat{V}$ (the operator coupling the reaction's initial and final electronic states) has been defined in terms of Coulombic or exchange interactions but always in the absence of a magnetic field,[49,55-57] one must add to it the electronic Zeeman operator (eq 11) when such an electron-transfer reaction takes place in the

$$V_{\mathrm{if}}(H) = \langle\Psi_{\mathrm{i}}|\hat{V} + \hat{\mu}H|\Psi_{\mathrm{f}}\rangle \qquad \hat{\mu} = \hbar\beta(k\hat{L} + g\hat{S})$$
$$\beta = \text{Bohr magneton} \qquad (11)$$

presence of such fields.[37,58] The dependence of the exponential factor on the magnetic field can be found by using the same arguments already considered in the deduction of eqs 3 and 4. It is possible to reduce eq 10 to a manageable one by introducing simplifications that are commonly used in the theoretical treatment of the magnetism in coordination complexes.[29,59] For example, the part of the exponential factor containing the activation susceptibility, $\delta\chi^{\ddagger}$, can be series expanded in powers of H while the electronic matrix element takes the form of a quadratic function of the field. The final reduction of eq 10 will be determined, however, by the multiplet nature of the ground state and the proximity of other electronic states, i.e., for all the levels achieving Boltzmann populations. In these regards, the diamagnetic nature of the reactants in eq 6, i.e., ignoring TIP contributions,[59,60] allows us to restrict the summation over the initial states in eq 10 to a single term, i.e., the reactants $^1\mathrm{A}_{1\mathrm{g}}$ ground states that remain unaffected by spin–orbit coupling and electronic Zeeman perturbations. If the series expansion in eq 10 is truncated to a polynomial with a fourth order dependence on the magnetic field, the ratio of the rate constants is given by eq 12.

$$k(H)/k(0) \simeq 1 + \{Q\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}2V_{\mathrm{if}}\mu_{\mathrm{if}}\}H + \left\{Q\sum_{\mathrm{i}}\alpha_1e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}\left[\mu_{\mathrm{if}}^2 + V_{\mathrm{if}}^2\frac{\delta\chi^{\ddagger}}{RT}\right]\right\}H^2 + \{Q\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}2V_{\mathrm{if}}\mu_{\mathrm{if}}\}\frac{\delta\chi^{\ddagger}}{RT}H^3 +$$
$$\{Q\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}\mu_{\mathrm{if}}^2\}\frac{\delta\chi^{\ddagger}}{RT}H^4 = 1 + aH + b\frac{\delta\chi^{\ddagger}}{RT}H^2 + a\frac{\delta\chi^{\ddagger}}{RT}H^3 + c\frac{\delta\chi^{\ddagger}}{RT}H^4 = 1 + a_1H + a_2H^2 + a_3H^3 + a_4H^4 \qquad (12)$$

This expression for $k(H)/k(0)$ can be used with the experimental results in Figure 1 and Table I in order to get information about the mechanism of the electron-transfer reaction. For example, values of the activation magnetic susceptibility (eq 13) and the Boltzmann-weighted electronic matrix element (eq 14) can

$$a_3/a_1 = \delta\chi^{\ddagger}/RT \qquad (13)$$

$$\left(a_2 - a_4\frac{a_1}{a_3}\right)\frac{a_1}{a_3} = Q\sum_{\mathrm{i}}\alpha_{\mathrm{i}}e^{-E_{\mathrm{i}}/RT}\sum_{\mathrm{f}}|V_{\mathrm{if}}|^2 = |\bar{V}|^2 \qquad (14)$$

be calculated from known values of the coefficients a_i, $i = 1, 2, 3$, and 4 (Table I). It must be noted that the $|\bar{V}|^2$ values and the calculated value of A in eq 10 give values in the order of 10^{10} for the preexponential factor. This observation suggests that the reaction in eq 6 is nearly adiabatic with a restriction factor, $f \sim 10^{10}/Z = 10^{-1}$, larger than one previously reported.[37] If one considers, however, the uncertainties and errors associated with each calculation, it is possible that the value of the restriction factor is between the following limits: $10^{-1} \geq f \geq 10^{-2}$. In these regards, we must consider two further aspects of the reactions reported above: the symmetry-determined selection rules for the coupling in the electronic matrix element (eq 10) and the behavior of the activation magnetic susceptibility, $\delta\chi^{\ddagger}$.

(b) Symmetry-Determined Selection Rules.[61] Fermi's Second Golden Rule, $k = (2\pi/\hbar)|\langle\Psi_{\mathrm{i}}|\hat{\mathcal{H}}_1|\Psi_{\mathrm{f}}\rangle|^2\,\rho\omega$ leads to the (master or absolute) selection rule[62,63]

$$\Gamma(\Psi_{\mathrm{i}}) \otimes \Gamma(\hat{\mathcal{H}}_1) \otimes \Gamma(\Psi_{\mathrm{f}}) = \Gamma_1 + ... \qquad (15)$$

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(58) In terms of the quantum-mechanical treatment of an outer-sphere electron transfer,[49] the transition probability from an initial state, Ψ_{i}, to a final state, Ψ_{f}, is $k = (2\pi/\hbar)|\langle\Psi_{\mathrm{i}}|\mathcal{H}_{\mathrm{et}}|\Psi_{\mathrm{f}}\rangle|^2$. The operator $\mathcal{H}_{\mathrm{et}}$ is the Hamiltonian for the electron-transfer process in the absence of an external magnetic field.[49] Inspection of eq 1 reveals that, in such a field's presence, the transition probability for an electron-transfer process is $k = (2\pi/\hbar)|\langle\Psi_{\mathrm{i}}|\mathcal{H}_{\mathrm{et}} + \hat{\mu}H|\Psi_{\mathrm{f}}\rangle|^2$ where $\hat{\mu}$ is the magnetic dipole operator. The procedure used in ref 49 for the factorization of the transition probability gives $k(H)_{\mathrm{if}} = (2\pi/\hbar)|V_{\mathrm{if}} + \mu_{\mathrm{if}}|^2G$, where V_{if} is an electronic coupling matrix element and μ_{if} is the transition magnetic dipole. The Franck–Condon factor, G, takes into account solvent and nuclear reorganizations in the electron transfer.

(59) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; Chapter 6, pp 139–149.

(60) In low-spin cobaltic complexes, there is paramagnetism independent of the temperature, TIP, associated with the second or high-frequency term in Van Vleck's formula.[58] However, TIP makes contributions with a magnitude of ca. 10^{-6} erg G^{-2} to the magnetic susceptibility, a value which is too small in comparison with other contributions discussed elsewhere in the text.

(61) Group theoretical treatments and related conventions follow: Piepho, S.; Schatz, P. *Group Theory in Spectroscopy*; Wiley-Interscience: New York, 1983.

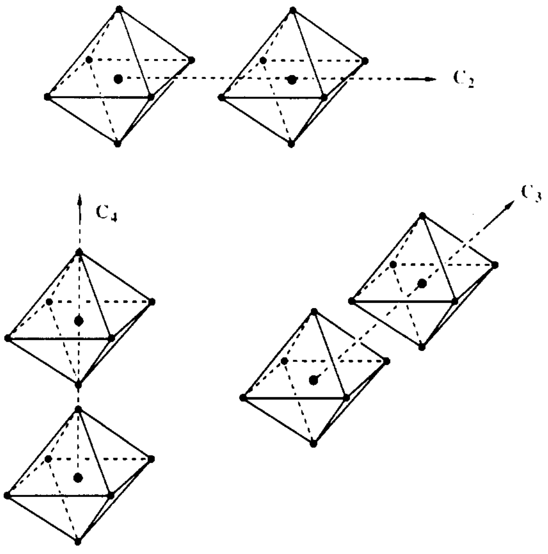

Figure 4. Relative orientations of two octahedra that preserve given symmetry elements of the O_h point group, i.e., the C_2, C_3, and C_4 rotation axes, used for calculations elsewhere in the text.

for processes whose lifetime, $\tau = 1/k$, must be finite. Equation 15 establishes that the direct product of the irreducible representations (irreps) for the complete eigenfunction of the initial state, $\Gamma(\Psi_i)$, the final state, $\Gamma(\Psi_f)$, and a set of Hamiltonian terms describing the evolution of the molecular system from the initial to the final state, $\hat{\mathcal{H}}_1$, must span the totally symmetric irrep, Γ_1 in the point group of the bimolecular reaction's encounter complex. More specific selection rules (eq 16) can be derived by considering

$$\Gamma(\phi_i) \otimes \Gamma(\hat{V}) \otimes \Gamma(\phi_f) = \Gamma_1 + ... \qquad (16)$$

that the electronic matrix element is a factor in the expression in eq 10 of the rate constant for outer-sphere electron transfers. In eq 16, $\Gamma(\phi_i)$, $\Gamma(\hat{V})$, and $\Gamma(\phi_f)$ are irreps of the eigenfunction for the initial electronic state, for the electronic coupling operator, and for the final electronic state respectively. It must be noted that the operator $\hat{V}$ has been already defined by other authors as an electrostatic interaction, exchange or Coulombic,[49-56] for the electron transfer between two metal centers and must be regarded, therefore, as an invariant scalar transforming like the totally symmetric irrep in the point group of the bimolecular system. If $\hat{V}$ does not operate over the spin eigenfunctions, it is possible to recast eq 16 in the form of eqs 17 and 18, where the

$$\Gamma(S_i) \otimes \Gamma(S_f) = \Gamma_1 + ... \qquad (17)$$

$$\Gamma(\varphi_i) \otimes \Gamma(\varphi_f) = \Gamma_1 + ... \qquad (18)$$

electronic wavefunctions in eq 16 have been written as products, $\phi_i = S_i\varphi_i$ and $\phi_f = S_f\varphi_f$, of the respective spin, S_i and S_f, and orbital, φ_i and φ_f, wave functions. In keeping with the eigenfunctions proposed in the literature for the description of the respective ground states of Co and Ru species,[53,55-56] the eigenfunctions for the species in the electron transfer between $Co(NH_3)_6{}^{3+}$ and $Ru(NH_3)_6{}^{2+}$ (eqs 19–22) can be expressed in a ket notation, where

$$\langle Co^{III}| = \langle Co^{III}; A_{1g}, 0| + \alpha\langle Co^{III}; T_{1g}, 1| + \alpha'\langle Co^{III}; CT, 1| \qquad (19)$$

$$\langle Ru^{II}| = \langle Ru^{II}; A_{1g}, 0| \qquad (20)$$

$$\langle Ru^{III}| = \langle Ru^{III}; T_{2g}, \tfrac{1}{2}| + \beta\langle Ru^{III}; T_{1g}, \tfrac{3}{2}| + \beta'\langle Ru^{III}; CT, \tfrac{3}{2}| \qquad (21)$$

$$\langle Co^{II}| = \langle Co^{II}; T_{1g}, \tfrac{3}{2}| + \nu\langle Co^{II}; E_g, \tfrac{1}{2}| \qquad (22)$$

Table II. Descent in Symmetry from an O_h and an O' Point Group Symmetry to the Point Groups of Two Encountering Octahedra[a]

Corresponding Orbital States

point group[b]			
O_h	C_{4v}	C_{2v}	C_{3v}
A_{1g}	A_1	A_1	A_1
E_g	$A_1 + B_1$	$2A_1$	E
T_{1g}	$A_2 + E$	$A_2 + B_1 + B_2$	$A_2 + E$
T_{2g}	$A_1 + E$	$A_1 + B_1 + B_2$	$A_1 + E$

Corresponding Spin States

O'	D'_4	D'_2	D'_3
(S = 2) E'_1	$A'_1 + B'_1 + B'_2 + E'_1$	$2A' + B'_1 + B'_2 + B'_3$	$A'_1 + 2E'_3$
(S = 1) A'_1	$A'_2 + E'_1$	$B'_1 + B'_2 + B'_3$	$A'_2 + 2E'_3$

[a] Point groups for the relative orientation of two octahedra shown in Figure 5, and states relevant to the species in eq 6. See also Table II. [b] The lifting of the orbital restrictions can be established from the direct product of the corresponding states, e.g. for $T_{1g} \otimes T_{2g}$ in O_h we have $(A_2 + E) \otimes (A_1 + E) = A_1 + 2A_2 + B_1 + B_2 + 2E$ in C_{4v}, $(A_1 + B_1 + B_2) \otimes (A_2 + B_1 + B_2) = 2A_1 + 3A_2 + 2B_1 + 2B_2$ in C_{2v} and $(A_1 + E) \otimes (A_2 + E) = A_1 + 2A_2 + 3E$ in C_{3v}. It must be noted that the angular momentum components span the irreps $\Gamma(\hat{L}_z) = A_2$ and $\Gamma(\hat{L}_x,\hat{L}_y) = E$ in C_{4v}, $\Gamma(\hat{L}_z) = A_2$ and $\Gamma(\hat{L}_x,\hat{L}_y) = E$ in C_{3v}, and $\Gamma/\hat{L}_z) = A_2$, $\Gamma(\hat{L}_x) = B_1$, and $\Gamma(\hat{L}_y) = B_2$ in C_{2v}.

α, α', β, β', and ν are the spin–orbit coupling coefficients providing the adequate amount of given excited states mixing into the species ground states. Moreover the triplet $\langle Co^{III}$; CT, 1| and quartet $\langle Ru^{III}$; CT, $^3/_2|$ charge-transfer states are expected to be those having the lowest energies and span, in the double group O', the same irrep of the respective Co(III) and Ru(III) ground states.

Since the point group of an encounter complex formed by two octahedra with identical or with different metal ions is not O_h, (Figure 4) the orientation of one octahedron with respect to the other can be expressed in terms of relative orientations that preserve some symmetry elements of the O_h group. The point group of the transition state in each of these configurations is a subgroup of the O_h (Figure 4).[64] Therefore, the electronic coupling operator $\hat{V}$ remains an invariant scalar only under the symmetry operations of each subgroup and the eigenfunctions for the octahedral species, eqs 19–22, must be projected into these subgroups in order to find the initial and final state functions coupled by the operator.[61,63] Preservation of the C_2, C_4, and C_3 rotations in the collision of two octahedra with different metal ions leads to transition states with symmetries belonging to the C_{2v}, C_{4v}, and C_{3v} point groups (or equivalent D'_2, D'_4, and D'_3 double groups), respectively (Table II). The descent in symmetry from O_h to such axial groups can be used, therefore, in the determination of those initial and final states that according to symmetry-established selection rules correspond to allowed crossings from reactants to products (Table II). In a rather crude statistical limit where only the allowed crossings in each configuration make contributions to the electronic matrix element (eq 10) and each crossing is weighted according to the number of configurations (Appendix), one can calculate a lower limit for the spin-orbital restriction, $f = {}^1/_{25}$, when the initial and final states of the reaction are formulated by the respective ground states of the reactants and the products. However, the reaction can generate $Co(NH_3)_6{}^{2+}$ in its electronic excited state, ^2E_g,[54] a reaction path those restriction, $f = {}^1/_6$, is in better agreement (than $f = {}^1/_{25}$) with calculations based on the empirically determined Boltzmann-weighted electronic coupling (eq 14).

The effect of the magnetic field on the reaction rate can be associated with nonvanishing matrix elements, $\mu_{if} = \langle\Psi_i|k\hat{L} + 2.0\hat{S}|\Psi_f\rangle$, where the initial and final states of the molecular system are coupled by the magnetic dipole operator. This transition magnetic dipole can be expressed as $\mu_{if} = \langle\{Co^{III}\}_i\{Ru^{II}\}_i/k\hat{L} + 2.0\hat{S}|\{Co^{II}\}_f\{Ru^{III}\}_f\rangle$, where each element in braces represents the electronic state of a given species, i.e., wave functions adapted to the symmetry of the encounter complex. When the electronic

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(62) Reference 28, p 103.

(63) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*; Pergamon Press: New York, 1974.

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state of each species is written as a product of an orbital and a spin function, i.e., ignoring intramolecular spin–orbit coupling, a path leading to ground-state products, $(^4T_{1g})Co(NH_3)_6^{2+}$ and $(^2T_{2g})Ru(NH_3)_6^{3+}$, or a path forming $(^2E_g)Co(NH_3)_6^{2+}$ has vanishing transition magnetic dipoles. This is not a surprising result because the reactants have nondegenerate ground states: a main difference from other reactions (eqs 8 and 9).

If wave functions are perturbed by intramolecular spin–orbit coupling, i.e., functions of the type described by eqs 19–22, the nondegenerate initial state can be written

$$\Psi_i = \langle\{Co^{III}\}\{Ru^{II}\}| = \langle Co^{III}; A_{1g}, 0|\langle Ru^{II}; A_{1g}, 0| + \alpha\langle Co^{III}; T_{1g}, 1|\langle Ru^{II}; A_{1g}, 0| + \alpha'\langle Co^{III}; CT, 1|\langle Ru^{II}; A_{1g}, 0| \quad (23)$$

Although the first term of eq 23 cannot be coupled by the magnetic dipole operator to the final state, the symmetry properties of the second and third terms allow such a coupling. When both products are formed in their ground states, some components of the multiplet

$$\Psi_f = \langle\{Co^{II}\}\{Ru^{III}\}| = \langle Co^{II}; T_{1g}, {}^3\!/_2|\langle Ru^{III}; T_{2g}, {}^1\!/_2|$$

satisfy a selection rule $\Gamma_i\Gamma_L\Gamma_f = \Gamma_1 + ...$, where Γ_L is the irrep span by the electronic angular momentum and Γ_1 is the totally symmetric irrep in the double group of the encounter complex. A similar reasoning can be used when the initial state (eq 23) is coupled to a final state

$$\Psi_f = \langle Co^{II}; E, {}^1\!/_2|\langle Ru^{III}; T_{2g}, {}^1\!/_2|$$

where the reaction product $Co(NH_3)_6^{2+}$ is formed in the ^2E_g excited state. In these regards, it must be concluded that intramolecular LS mixing of excited states into the ground state of the reactants must determine in a large extent the value of the transition magnetic dipoles and the intensity of the magnetodynamic effects.

(c) Activation Magnetic Susceptibilities. In such reactions where the magnetic field has a negligible effect on the energy of the initial states, e.g., the reactants are diamagnetic and the transition magnetic dipole, μ_{if}, is small in comparison with the electronic coupling, V_{if} in eq 11, the activation magnetic susceptibility can be calculated from the known values of $\delta_T = (k(H)/k(0))_T$, where subscripts specify the temperature. Since values of $\delta\chi^{*}_{298}$ and $a_{1,298}$ were known from measurements of the rate constant of various field intensities (Table I), we calculated $\delta\chi^{*}_T$ at other temperatures T with an iterative method.[34] Trial values of $a_{1,T}$ at temperatures slightly above or below 298 K were calculated by replacing values of $a_{1,298}$ and ρ_T in eq 24. New values of $\delta\chi^{*}$ were calculated by using these trial values of $a_{1,T}$ with eq 25, and

$$a_{1,T} = \frac{1}{H}\left[\rho_T - 1 - \frac{\delta\chi^{*}_T}{RT'}H^2\right] \qquad (24)$$

$$\delta\chi^{*}_T = \frac{\rho_T - 1 - a_{1,T}H}{(1 - a_{1,T}H)H^2}RT' \qquad (25)$$

then replaced in eq 24. The procedure was repeated until the difference between the results of two consecutive cycles was less than 10%. Moreover, the results of a calculation were used as trial values for calculations with rate constants measured at slightly different temperatures.

The results of calculating $\delta\chi^{*}$ for the reaction of $Co(NH_3)_6^{3+}$ with $Ru(NH_3)_6^{2+}$ (Figure 5) signal that the transition state of the reaction is paramagnetic despite the reactants diamagnetism. Indeed, the two reactants have small and negative magnetic susceptibilities that are characteristic of diamagnetic complexes, and the large positive values of $\delta\chi^{*}$ must be assigned, in accord with its definition in eq 5, to the activated complex, i.e., χ^{*}. Conversion of χ^{*} to an effective magnetic moment of activation, EMMA, reveals that the values of EMMA are larger than the combined momenta of the paramagnetic products, e.g., $(^4T_{1g})$-$Co(NH_3)_6^{2+}$ and $(^2T_{2g})Ru(NH_3)_6^{3+}$.[65] The absence of additivity in the coupling of the momenta could also be a manifestation of a very strong LS mixing of electronic states in the encounter complex.

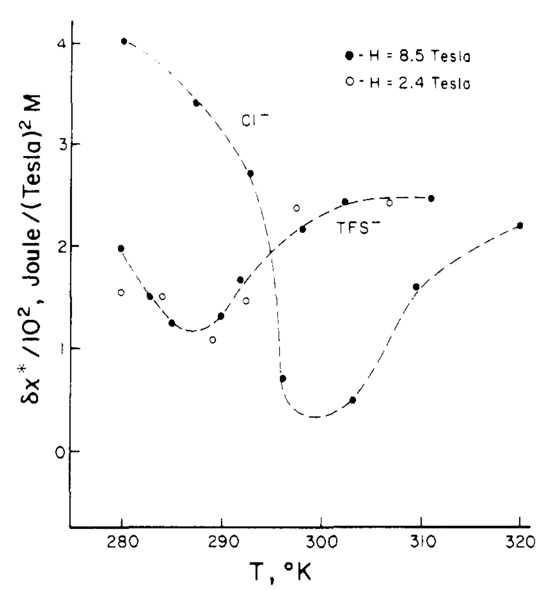

Figure 5. Dependence of $\delta\chi^{*}$ on the temperature for reactions of $Co(NH_3)_6^{3+}$ with $Ru(NH_3)_6^{2+}$ under ionic strengths I = 0.3 M NaTFS or I = 0.3 M NaCl, respectively. For other conditions, see Figure 1.

A further feature of $\delta\chi^{*}$ is that the functional dependence on the temperature is specific for the counterion, i.e., Cl^- or triflate, as has been reported above for the dependence of $k(H)/k(0)$ on H (Figure 1). Such a specificity appears to be related more to the ability of Cl^- to impart charge-transfer character into the ground state, i.e., from an ion-pair change-transfer state, than to steric reasons. Such a mixing of charge-transfer states into the ground state must be, at least in part, magnetic-field dependent, e.g., as expected for Zeeman-induced mixing, and its contribution to the value of $k(H)/k(0)$ reaches a significant magnitude for fields $H > 5$ T. The magnetic-field perturbation of the rate of the reaction with $Co(NH_3)_5Cl^{2+}$ (eq 7) is in agreement with these considerations about the participation of charge-transfer states.

Conclusions

The observations reported in this work have been rationalized in terms of existing theories for the rate of outer-sphere electron-transfer reactions. Such theories were modified by incorporating in them various interactions with the magnetic field. They have been applied to reactions involving diamagnetic reactants and remain to be tested with more complex systems incorporating paramagnetic reactants. It must be noticed, however, that the strong paramagnetism associated with the transition state has been found in reactions with para- and diamagnetic reactants. The origin of the transition-state paramagnetism must be further investigated on a broader experimental base. It is also clear that magnetodynamic effects on electron-transfer reactions between coordination complexes cannot be properly treated by the radical-pair model.[66] This is, however, not surprising if one accepts that the properties of a transition-metal coordination complex seldom approach those of organic radicals, a point that can be extended to the mechanism of their reactions. Our results also show that, in these reactions, studies carried out at weak fields (less than a tesla), fail to give a complete picture of the magne-

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(65) The EMMA, μ^{*}_{eff}, can be conveniently defined in the same manner of the "magnetic moment",[29] and the activation magnetic susceptibility, $\mu^{*}_{effT} = (3k/N\beta^2)^{1/2}(\delta^{*}T)^{1/2} = 2.828(\delta^{*}T)^{1/2}$, for diamagnetic reactants. It must be noted that the large values of EMMA, larger than those for most of the paramagnetic materials, should probably be viewed as an intrinsic property of the transition state.[30] Does this paramagnetism approach the one in a charge-transfer state? This and other quadaries of the magnetodynamic effects must be resolved with more experimental work in these chemical systems.

(66) Steiner, U. E.; Wolf, H.; Ulrich, Th.; Ohno, T. *J. Phys. Chem.* **1989**, *93*, 5147.

todynamic effects on reactions of coordination complexes; mechanisms derived from such a narrow experimental base must be considered in error.

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Appendix

The approach for calculating orbital and spin restrictions is based on the assumption that, in each particular orientation of the two octahedra, each of the allowed crossings, i.e., one preserving the electronic state symmetry, from the initial to the final electronic state makes a unity contribution to the prohibition factor while each of the forbidden crossings (in a zero order) makes a negligible contribution. The factors must, however, be calculated by dividing the number of effective crossings (crossings with unity contributions) by the total number of crossings, i.e. allowed and forbidden crossings. In these regards, each orientation of the octahedra (Figure 4 and Table II) having a C_{4v} point group symmetry can make only $^1/_9$ contribution according to the orbital prohibition and $^1/_5$ contribution according to the spin prohibition. Indeed, for products with electronic states T_{1g} and T_{2g}, respectively, only one path from E·E (Table II) spans A_1 and correlates, therefore, with an A_1 state of the products. If one uses a similar rationale, a configuration with a C_{2v} point group symmetry contributes $^2/_9$ (orbital contribution) and $^2/_5$ (spin contribution) while one with a C_{3v} point group symmetry contributes $^1/_9$ (orbital contribution) and $^1/_5$ (spin contribution). Insofar as the probability of achieving a given configuration is proportional to the multiplicity of the symmetry preserved in the octahedra collision, the transmission coefficient can be expressed

$$f = \frac{\sum\limits_{\mathrm{i}} n_{\mathrm{i}} o_{\mathrm{i}} \sigma_{\mathrm{i}}}{\sum\limits_{\mathrm{i}} n_{\mathrm{i}}} = \sum_{\mathrm{i}} \frac{n_{\mathrm{i}}}{n} o_{\mathrm{i}} \sigma_{\mathrm{i}}$$

where n_{i} is the number of configurations preserving a given symmetry element identified by the subscript i, o_{i} and σ_{i} are the orbital and spin contributions considered above. Substitution of the values in this expression leads to

$$f = \left[\frac{1}{9} \times \frac{1}{5} \times \frac{2}{5}\right]_{C_{4v}} + \left[\frac{2}{9} \times \frac{2}{5} \times \frac{1}{5}\right]_{C_{2v}} + \left[\frac{1}{9} \times \frac{1}{5} \times \frac{2}{5}\right]_{C_{3v}} \sim \frac{1}{25}$$

Spin–orbit coupling can lift some spin restrictions, and this number must be considered, therefore, a lower limit. Moreover, it is possible to assume that $Co(NH_3)_6{}^{2+}$ can be generated in its ^2E_g excited state while $Ru(NH_3)_6{}^{3+}$ is in its ground state.[54] One can calculate $f = {}^1/_6$ for such a reaction path with the same rationale discussed above.

Registry No. $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $Co(NH_3)_6{}^{3+}$, 14695-95-5; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(en)_3{}^{3+}$, 14878-41-2; $Co(sep)^{2+}$, 63218-22-4.

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Molecular Topology and Exchange Interaction: Synthesis and Magnetic Properties of $[Cu^{II}{}_3M^{II}]$ (M = Cd, Ni, Mn) Tetranuclear Species

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Three tetranuclear complexes of formulas $[\{Cu(oxpn)\}_3Cd](NO_3)_2{\cdot}2H_2O$, $[Cu_3Cd]$, $[\{Cu(oxpn)\}_3Ni](ClO_4)_2{\cdot}2H_2O$, $[Cu_3Ni]$, and $[\{Cu(oxpn)\}_3Mn](ClO_4)_2{\cdot}2H_2O$, $[Cu_3Mn]$, where $oxpn^{2-}$ is *N,N'*-bis(3-aminopropyl)oxamidato have been synthesized. Magnetic susceptibility and EPR measurements in the 4.2–3.00 K temperature range have been carried out for this series of complexes. The magnetic data have been interpreted by using the Heisenberg Hamiltonian and lead to J values equal to −1.45, −101.0, and −26.6 cm^{-1} for $[Cu_3Cd]$, $[Cu_3Ni]$, and $[Cu_3Mn]$. The relation between the local **g** tensor and the observed average g values is analyzed. A discussion about the relative interaction intensity in such a series of complexes is presented. Finally, the nature of the ground state is discussed in relation to the topology and the spin values of the metal ions.

Introduction

A lot of work has been devoted to the study of the exchange interaction in polymetallic systems. One of the challenges of this field is the design of complexes with predicted magnetic properties.[2] To achieve this goal, the influence of parameters such as the symmetry of magnetic orbitals,[3,4] the nature of the bridging or terminal ligands,[2,5–6] and small geometrical changes[8,9] has been studied. Surprisingly, no study of the influence of the molecular topology on the magnetic properties of inorganic complexes has been done. On the other hand, organic chemists attempting to synthesize high-spin molecules have been extremely interested in this subject.[10,11] For instance, it is well-known that the trimethylenemethane biradical has a triplet ground state due to its topology.[10,12] A similar topology for inorganic complexes is scarce although the diamagnetic Werner brown salt $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ [13] where en is 1,2-diaminoethane has been known since 1907. The synthesis of the chromium analogue of Werner's complex by Andersen and Berg a few years ago[14a,b] provided

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(1) (a) Universitat de València. (b) Université de Paris-Sud.

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